Thesis Changes Log

Name of Candidate: Pramod Mulbagal Rajanna

PhD Program: Physics

Title of Thesis: Hybrid heterojunction solar cells using single-walled carbon nanotubes and amorphous silicon thin films

Supervisor: Prof. Albert G. Nasibulin (Prof. Peter D. Lund – Aalto University)

Chair of PhD defense Jury: Prof. Nikolay Gippius ***Email:*** *n.gippius@skoltech.ru*

Date of Thesis Defense: 27 May 2020

The thesis document includes the following changes in answer to the external review process.

Dear Jury members, 14 May 2020

First, I would like to thank you for considering my work and evaluating it scientifically and technologically by providing useful comments and queries to improve the thesis. I have addressed all the comments and made necessary changes in the thesis. The response to your comments are as explained below.

Thank you very much!

Best Regards
Pramod M. Rajanna

Reply to Prof. Dmitry Paraschuk comments

(1) General

Q. A brief introduction and summary of all results of the thesis before section 4.1 would improve the presentation. Also, I would recommend giving a short conclusion with implications at the end of section 4.1.

Answer: Thank you for your suggestion. A brief introduction and summary of the results is presented in page 39 (before section 4.1). The text has been modified as follows:

"In this section, the results obtained in the development of a conductive p-type SWCNT transparent conductor and its application in hybrid heterostructure solar cell based on amorphous silicon is discussed. At the beginning, the results obtained for quantitative measurements of the adhesion of SWCNT films with substrate materials in air and inert Ar atmosphere using atomic force microscopy is presented. It is found that adhesion of SWCNT films depends on the atmospheric conditions under which it is stored and de-posited on a substrate material. Following this, a simple fabrication method of hybrid heterostructure solar cells is proposed in which the SWCNT-

PEDOT:PSS composite p-type film forms a coupled continuous hybrid hetero-junction with a-Si:H absorber. The opto-electrical properties of this composite is extensively characterized and further optimized by introducing multifunctional components like ultrathin MoO3 and SWCNT fibers. Finally, a rationally designed p-type transparent conductor is proposed with a state-of-the-art sheet resistance of 17 Ω/sq at 90% transmittance. Integrating the developed p-type transparent conductor as a window layer and top electrode on a-Si:H in a nip configuration resulted in a dramatic 16% increase in its power conversion efficiency reaching up to 8.8%."

As suggested, a short conclusion is added at the end of section 4.1. The text is modified as follows on page 43:

"To summarize, through experimental observations it can be stated that the adhesion is greatly influenced by the environmental conditions and surface functionalization. It is observed that the SWCNT films have a better adhesion in an inert Ar atmosphere. However, the adhesion affected by storing the samples under ambient conditions can be greatly improved by a simple HF-treatment. This provides new insight into the physical mechanisms of SWCNT thin film adhesion that will be useful for its successful implementation in carbon nanotube based devices."

Q. Doping of SWCNT by PEDOT:PSS (p. 35, p.41). The statement that PEDOT:PSS dopes SWCNT does not seem conclusive from the thesis. Why should PEDOT:PSS dope SWCNT? The observation that the work function of the composite is between those of PEDOT:PSS and SWCNT seems to be not enough. Moreover, if the surface of the composite is PEDOT:PSS (Fig. 4-5), I would expect that KPFM probes PEDOT:PSS and not SWNT. The discussion on this should be extended.

Answer: Every single carbon atom in SWCNTs is on the surface exposed to the environment. Therefore, any atom/molecule put on a SWCNT causes changes in their electronic structure and charge transfer between the atom/molecule and a nanotube[1,2]. Therefore, when PEDOT:PSS is injected on the SWCNT film, the charge carriers are transferred, thereby doping the SWCNTs and resulting in decreased sheet resistance as in Figure 4-4. Further, the KPFM measured work functions are similar to the ultraviolet photoemission spectroscopy measured values as reported by Fan *et al.* [3].

The text has been accordingly revised on Page 44 as follows:

"Fan *et al.* reported similar values of work functions measured by ultraviolet photoemission spectroscopy [97]", and "every single carbon atom are on the surface exposed to the environment. Therefore, any atom/molecule put on a SWCNT cause changes in their electronic structure and charge transfer between the atom/molecule and a nanotube. Therefore, when PEDOT:PSS is injected it filled micropores in the SWCNT film and, that the holes in the PEDOT:PSS patches can transfer to the interconnected SWCNT network consequently, doping the SWCNTs [56,57,97]".

References:

[1] Kim KK, Yoon SM, Park HK, Shin HJ, Kim SM, Bae JJ, et al. Doping strategy of carbon nanotubes with redox chemistry. New J Chem 2010. https://doi.org/10.1039/c0nj00138d.
[2] Ki KK, Jung JB, Hyeon KP, Soo MK, Geng HZ, Kyung AP, et al. Fermi level engineering of single-walled carbon nanotubes by AuCl 3 doping. J Am Chem Soc 2008. https://doi.org/10.1021/ja8038689.
[3] Fan Q, Zhang Q, Zhou W, Xia X, Yang F, Zhang N, et al. Novel approach to enhance efficiency of hybrid silicon-based solar cells via synergistic effects of polymer and carbon nanotube composite film. Nano Energy 2017.

https://doi.org/10.1016/j.nanoen.2017.02.003.

Q. Why may a strong blue shift arise from strong absorbance of SWCNT? (p. 38). On p. 40, the discussion on blue shift is not self-consistent. On the one hand, the doctoral candidate discusses a blue shift for CNT20; on the other hand, "the shape of the EQE spectra" does not change with SWCNT film thickness. This discussion should be revised.

Answer: The explanation for the blue shift is as follows:

The shift mainly arises due to optical and electrical changes. SWCNTs have absorbance in the whole spectral range (near UV to far IR, 170 to 3000 nm) with a strong plasmon peak near 250 nm as shown below in Figure 1. In our cell structure, the a-Si:H (n~4) is sandwiched between lower refractive index (n) materials (PEDOT:PSS-SWCNTs composite, $n_{PEDOT:PSS}$ = 1.2 and n_{SWCNT} = 1.09) and Al doped ZnO (n_{AZO} = 2) thereby causing interference. When the light is incident on the solar cell, it passes through a stack of layers with different refractive index. With each passing layer, the incident light transmits through much reduced intensity and phase shift at every incident wavelength. This follows similar as Fabry-Perot interferometer. Therefore, this shift at each wavelength results in a strong blue shift as observed in the external quantum efficiency spectra. Moreover, in Figure 4.7c for SWCNTs/a-Si:H HSC, the SWCNTs film have a non-uniform contact with underneath a-Si:H creating voids, which are filled with the insertion of PEDOT:PSS in the SWCNTs network (as shown in surface morphological SEM Figure 4-5). This results in a continuous junction with improved interface and reduced recombination. This is clearly seen in Table 4-1, with higher V_{oc} values for PEDOT:PSS-SWCNT/a-Si:H HSC when compared to SWCNTs/a-Si:H or PEDOT:PSS/a-Si:H.

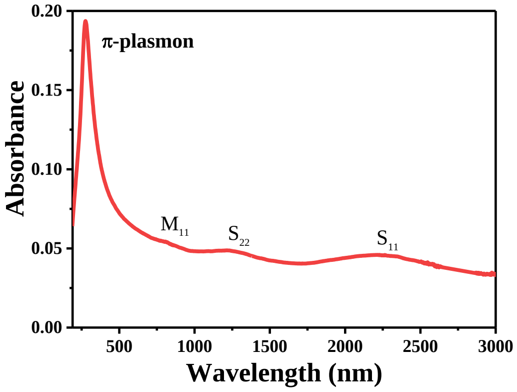

Figure 1. Absorbance spectra of SWCNT thin film utilized for adhesion studies

The text has been accordingly modified on Page 48 as:

"Additionally, the SWCNT/a-Si:H solar cell shows a strong blue-shift which may arise from the strong absorbance of SWCNTs near 250 nm [54] and phase shift of incident wavelength caused by stack of different refractive index materials in the solar cell. Moreover, in Figure 4.7c for SWCNTs/a-Si:H HSC, the SWCNTs film have a non-uniform contact with underneath a-Si:H creating voids, which are filled with the insertion of PEDOT:PSS in the SWCNTs network (as shown in surface morphological SEM Figure 4-5). This results in a continuous junction with improved interface and reduced recombination. This is clearly noted in Table 4-1, with higher Voc values for PEDOT:PSS-SWCNT/a-Si:H HSC when compared to SWCNTs/a-Si:H or PEDOT:PSS/a-Si:H."

The discussion is also modified on Page 50 as:

"Figure 4-8b shows the experimental EQE spectra corresponding to various SWCNT thicknesses in HSCs. It can be observed that the EQE value decreases with increase in the SWCNT films thickness, with a maximum EQE value of 42% at 514 nm obtained for CNT20. This is caused by lower absorption in the composite film (p-layer) and reduced recombination at the a-Si:H/SWCNT interface in CNT20 compared with any other sample. The current density was calculated from EQE (as described in section 3.7) for all the fabricated solar cells. The current density values of all the solar cells from the J-V curve and EQE match closely. For CNT10, CNT40, CNT60, and CNT80 the EQE dramatically decreases for wavelengths shorter than 350 nm indicating a strong surface recombination at the i:a-Si:H/SWCNT interface. A sharp fall in the EQE for all SWCNT film thickness beyond 700 nm can be attributed to the a-Si:H energy gap (1.7 eV). This spectral behavior resembles that of a-Si:H nip solar cells, indicating that the photo generation process goes on mainly within the i:a-Si:H."

Q. PMMA as an AR layer (p. 43). The statement that PMMA works as an AR layer needs justification, or, otherwise, it should be presented as an explanation of the data. The statement should be supported by calculation (estimations) from the optical thickness (or/and experiments with various thickness) to understand which thickness would be optimal.

Answer: The reflectance measurements have been carried out in detail and reported in Publication 2. The text has been modified on Page 53 and 54 as follows:

"Furthermore, the use of PMMA as an AR coating and encapsulant has been a topic of interest and several works have focused on the use of a PMMA layer acting as a broad band ARC over Si-CNT solar cells [105–107]. Hence, diffuse reflectance measurements were carried out to test the effect of PMMA as an ARC in our solar cell. The reflectance spectra of plain a-Si:H, a-Si:H with SWCNTs, a-Si:H with PEDOT:PSS, HSC without PMMA, and HSC with PMMA are shown in Figure 4-9c. The a-Si:H surface with textures exhibits about 20% minimum reflectance ranging from 500–800 nm. The reflection minima of the HSC without PMMA are slightly lower than those of plain a-Si:H, at about 16% in the visible region. The minimum reflectance of a-Si:H with PEDOT:PSS and a-Si:H with SWCNTs is lower than that of plain a-Si:H and is similar to the reflectance of HSC without PMMA. Further, HSC with PMMA shows a reduc-tion to about 4.5% reflectance in the visible region. Consequently, PMMA as an effective ARC increases the light trapping efficiency, producing more photo-generated carriers and thus increasing the current density and HSC efficiency."

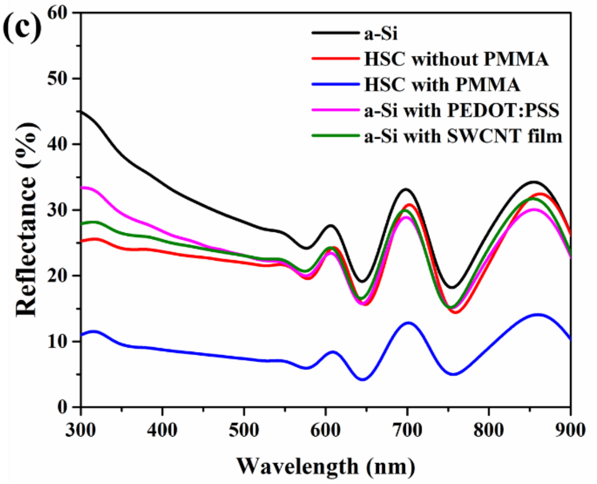

Figure 4-9. **(c)** Reflectance spectra of plain a-Si:H, HSC without PMMA, HSC with PMMA, a-Si:H with PEDOT:PSS, and a-Si:H with SWCNT film.

Q. Which simulations of J-V curves and EQE were done? (section 4.3.3)

Answer: Numerical simulations was carried out by our collaborator (DLR Institute, Germany) using AFORS-HET (automat for simulation of heterostructures) software. The details of the simulation are in Publication 3.
The text is modified in Section 4.3.3, Page 60 as follows: "numerical simulations carried out using AFORS-HET (automat for simulation of heterostructures) software."

Q. In section 4.3.3, the doctoral candidate compares the performance of HSC with the reference a-Si:H cell (PCE=7.5%). It would be nice to discuss why this PCE is below the best a-Si:H cells (PCE>10%).

Answer: We received the a-Si:H structures till the intrinsic absorber (from collaborator, DLR Institute, Germany) for which the reference cell produced in their baseline process production line had PCE of stable 7.5%. The hybrid heterostructure solar cells using the proposed TCF was fabricated with the received a-Si:H samples. It is to be kindly noted that the reference a-Si:H cell produced for this work was at lower deposition temperature (< 200 °C), without any back reflector, special texturing etc. Moreover, the goal of this thesis was not to produce world record a-Si:H solar cells. In this study, we used simple low temperature processes to establish a proof of concept with SWCNTs as p-type transparent conductor.

The text is modified on section 4.3.3, Page 61 as follows:

"It is to be noted that the reference cells are produced at substrate temperatures less than 200 °C, without any back reflector, texturing and other special processes as carried out for record a-Si:H solar cells."

Q. It might be appropriate to discuss the potential for scaling of the proposed TCFs.

Answer: The scaling of the proposed TCFs is the ultimate goal. But, for that to happen successfully, it is necessary to address several scientific and technological bottlenecks. They include: synthesis of reproducible and uniform SWCNTs, uniform doping of SWCNTs over large area samples, stability of conductive polymers, and finally a stable encapsulant.

The text is modified on Page 65 as follows:

"It is envisaged that the outcomes of this work will secure the future development of novel p-type TCFs in combination with the use of pure high quality semiconducting or metallic SWCNTs that are aligned with better passivation, improved doping stability of SWCNTs, light trapping schemes and nanostructuring that can potentially improve future photovoltaic devices."

(2) Minor methodical issues

Q. Section 3.7. Jsc calculation from EQE (without light bias) will be equal to Jsc from I/V curves, if Jsc depends linearly on the light intensity. This assumption should be mentioned.

Answer: The text has been modified in section 3.7 as: with the assumption that the $J_{sc}^{EQE\lambda}$ without light bias will be equal to the J_{sc} from J-V curve.

Q. p. 32, the method of thickness calculation of SWCNT films from thier optical transmittance should be mentioned. Also, it should be explained how the AFM thickness was measured on not continuous (mesh) films (SWNT).

Answer: The thickness of the SWCNT films calculated from their absorbance is given by: Thickness (nm) = 417 × Absorbance$_{550\ nm}$. The details are given in Mikheev, G. M.; Nasibulin, A. G.; Zonov, R. G.; Kaskela, A.; Kauppinen, E. I. Photon-Drag Effect in Single-Walled Carbon Nanotube Films. Nano Lett. 2012, 12 (1), 77−83.

The text is modified on Page 43 as "(as described in section 3.1)" and section 3.1, Page 31 as follows: "In addition to that, the film thickness can be easily estimated when the absorbance is known as following: Thickness (nm) = 417 × Absorbance550 nm [67]."

Using AFM: The SWCNT films were dry-transferred on Si wafer. A scratch was made and step was measured. A total of 50 data points were collected for statistics at different locations of the sample. The average was determined as approximate thickness.
The text is modified on Page 43 as follows: "The SWCNTs film transferred on Si wafer was densified using iso-propanol and allowed to dry till the solvent evaporation. A scratch was made on the SWCNTs film surface to measure the thickness using AFM. The thickness was averaged over 50 measured points."

Q. p. 57, which equipment was used for bending experiments?

Answer: The text is modified on Page 58 as "in an in-house developed bending setup". The details are as follows (given in Publication 4):

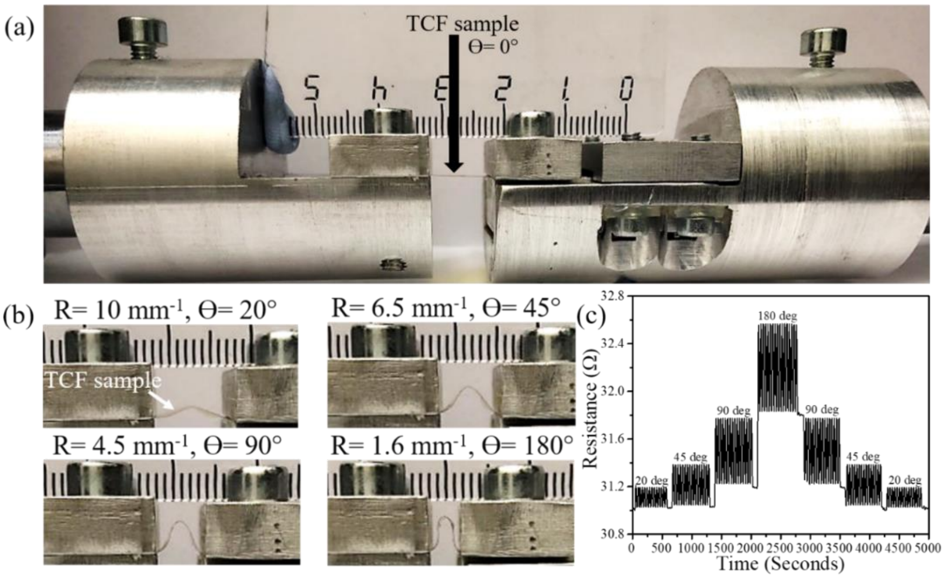

Figure S3. Mechanical flexibility tests of the TCFs: **(a)** Experimental setup to test flexibility; **(b)** Close-up of TCF behavior at bending angles of 20°, 45°, 90° and 180° with the corresponding calculated radius of curvature (R) in mm^{-1}; **(c)** Cyclic TCF4 resistance change at different bending angles.

Q. p.51, what was a reflective rear mirror?

Answer: A plain aluminum coated mirror was used as a reflective rear mirror. The text is modified on page. 60 as follows: "Introducing a plain aluminum coated reflective mirror on the back side"

(3) Other minor issues

Q. Abstract: using optical and electrical instead of "opto-electrical" seems to be more relevant, NIP abbreviation should be defined.

Answer: The suggestion has been addressed and accordingly the text has been revised in the abstract as optical and electrical. NIP and PIN are solar cell structure configurations.

Q. p.5, abbreviation Al:ZnO does not fit AZO in the text.

Answer: The abbreviation is changed to Al:ZnO throughout the thesis.

Q. p. 13, I am not sure that the candidate should self-evaluate his work ("impressive results").

Answer: The sentence has been revised on Page. 20 as: the results achieved in this project were motivating.

Q. p. 15, unclear statement: "a-Si:H has a higher absorption edge…than c-Si"; it is better to use the term charge-carrier mobility or charge mobility, but not just mobility; inaccurate statement: "light above the absorption edge".

Answer: The sentence is revised on Page. 23 as suggested to: 'The a-Si:H has a larger mobility gap and optical absorption coefficient than c-Si;; and 'light that is ≥E_{mob}'.

Q. p.20, the work function of MoO3 should be given with appropriate literature references. Deposition methods of MoO3 worth to be mentioned.

Answer: The work function of MoO_3, its deposition methods and relevant references are mentioned in section 2.5, page. 29 as: 'In the past few years, the high work-function of MoO_3 (6.5 to 6.8 eV) commonly deposited by thermal evaporation, sputtering, and atomic layer deposition has been successfully used as a hole-injection and –extraction material in solar cells which creates a large built-in voltage [18, 61-64].'

Q. p.26, the last but one line, what is the dark current at the short-circuit conditions?

Answer: The short-circuit condition is the maximum current, at zero voltage. Ideally, if V=0, $I_{sc} = I_L$. Note that I_{sc} is directly proportional to the available sunlight. In dark-state condition, as there is absence of light, I_{scdark} will be close to 'zero'. The text is modified on Page 35 as "(close to zero in absence of light)."

Q. p.36, the 3rd paragraph from the bottom, the last sentence. I suppose that the author means not "PEDOT:PSS HSC".

Answer: It has been corrected and revised on Page. 46 as PEDOT:PSS/a-Si:H HSCs.

Q. p.38, the text in the first line should be edited.

Answer: The text has been revised on Page 46 as: 'Subsequent to annealing rectangular shaped front contacts were made at the edges using silver paste on SWCNT/a-Si:H and PEDOT:PSS/a-Si:H HSC structures, respectively'.

Q. p. 39, what was the thickness of CNT10-CNT100?

Answer: The approximate thickness of the used SWCNT films are as mentioned in the sample nomenclature as CNT10 (~10 nm), CNT20 (~20 nm), CNT40 (~40 nm), CNT60 (~60 nm), CNT80 (~80 nm), and CNT100 (~100 nm).

The text is modified on Page 49 and 50 as follows: "(10 nm, 20 nm, 40 nm, 60 nm, 80 nm, and 100 nm samples named CNT10, CNT20, CNT40, CNT60, CNT80, and CNT100, respectively)"

Q. p. 40, not a good style "during the analysis.."; the 2nd paragraph, what does the author imply in "This might be" (strong blue response or decreased EQE with thickness)?; the equation does add nothing (it can be removed) as it was mentioned in Methods; why was Isc(EQE) calculated only for CNT20?

Answer: The sentence has been revised in Page. 50 as: "Moreover, from the *J-V* parameters in Table 4-2." This implies that the EQE value decreases with an increase in SWCNT thickness due to increased absorption. The sentence has been revised on Page. 50 as "The current density was calculated from EQE (as described in section 3.7) for all the fabricated solar cells." The sentence has been revised on Page 50 as: 'The current density values of all the solar cells from the J-V curve and EQE match closely.'

Q. p.42 and other places, drop-cast (not casted); italic "and" seems to be a format issue, and the statement is not clear: all the three parameters showed a 10% increase or only PCE?

Answer: A common term as drop-cast is used throughout the thesis. The 'and' is revised on Page. 52. The 10% increase is in the EQE saturation value for the sample without PMMA (EQE saturation value is 42%) and with PMMA (EQE saturation value is 47.1%).

Q. p.43, it would be much better to formulate explicitly the idea of doping SWNT by MoO3 with appropriate references (if relevant).

Answer: Doping of SWCNTs by MoO_3 is mentioned in Page. 57 with relevant references as: 'A similar observation was reported in several studies indicating that MoO3 is a stable dopant to SWCNTs [110–112].'

Q. p.45, the title of section 4.3.2 is not accurate, it seems to be "Optical, electrical, and …"

Answer: The title has been revised as suggested on Page. 56 as: 'Optical, electrical, and mechanical properties'.

Q. p. 51, in the sentence "The J-V …" "under AM1.5 conditions" should be deleted (as the figure shows also the dark curves), or one can remove the panel with the dark curves.

Answer: The sentence has been revised on Pg. 60 as 'The J-V characteristics of four different cell types under AM 1.5 and dark conditions are shown in Figures 4-12a and tabulated in Table 4-5.'

Q. It would be nice to update Ref.8.

Answer: The reference is updated on Page 66 as: 'Green MA, Dunlop ED, Hohl-Ebinger J, Yoshita M, Kopidakis N, Ho-Baillie AWY. Solar cell efficiency tables (Version 55). Prog Photovoltaics Res Appl 2020. https://doi.org/10.1002/pip.3228.'

Reply to Jury Member (Prof. Pavel Troshin) comments

1) Section 1/section 2.3: I recommend author to describe more clearly the nature of SWCNTs. State the nature and the typical ratio between metallic and semiconducting tubes, explain p-type doping mechanism of semiconducting tubes. Otherwise, terminology such as “p-type conductor or semi-metal” looks very confusing. Showing band structure of the pristine and doped SWNTs might be worthy.

Answer: The suggestions has been addressed in Section 2.3, page 26, 27, and 28 as follows:
All the SWCNTs film used in this thesis were synthesized by the aerosol (floating catalyst) method and consist of 1/3 metallic or 2/3 semiconducting nanotubes; therefore the have a certain bandgap and chirality, that influences its electrical and optical properties [49]. The statistical fractioning of randomly oriented SWCNTs in films limits the conductivity by the introduction of Schottky barriers between the nanotube contacts, which leads to contact resistance that cannot be overcome without further modification process [49].

Doping: SWCNT films reveal various outstanding optical and electronic properties but still have an issue with the reductiyon of Schottky barrier between semiconducting and metallic nanotubes. This has led to several processing methods to increase their optoelectronic characteristics. The techniques are based on the shift of the Fermi level (E_F for metallic (M) or semiconducting (S) nanotubes) position. In pristine nanotubes the E_F is usually located in the middle of density of states (DOS). Therefore, if the electrons or holes are added to SWCNTs, the E_F is shifted upward (n-type doping) or downward (p-type doping), compared to the initial position (Figure 2-3a and b), and conductivity increases. Normally, due to the presence of oxygen in the atmosphere, nanotubes become p-type doped, which is again related to the shift of E_F under ambient conditions.

Among several key strategies to modify the charge carrier type (substitutional doping, doping in an electrostatic field, work function change ($\Delta\Phi$) when connected to the metal, ambipolarity, etc.), the adsorption doping has numerous advantages [54,55]. The feasibility reason for this method is the exposure of all carbon atoms of SWCNTs to the environment. In this way, any atom/molecule put on a SWCNT causes charge transfer between the atom/molecule and a nanotube [56,57]. Thus, the selection of an appropriate chemical dopant that will be put on the SWCNTs is highly important to achieve the desired conductivity. Chloroauric acid ($HauCl_4$) and gold chloride ($AuCl_3$) are the chemical dopants used in this study as reported [54,56].

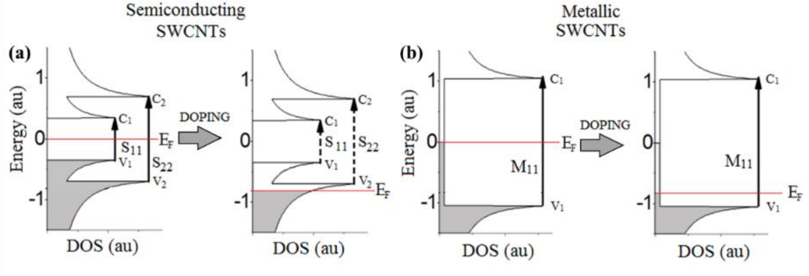

Figure 2-3. Density of states (DOS) of pristine and doped **(a)** semiconducting; and **(b)** metallic SWCNTs, respectively.

2) PEDOT:PSS was extensively used in this study. There are many different commercial formulations of this material with completely different properties (tens of products existing). However, I was not able to find information on the type(s) of the used PEDOT:PSS in the methodology part of the thesis. Providing this information is crucially important.

Answer: The suggestion has been addressed in section 2.4, page 28 as follows:

In this study, PEDOT:PSS was used from the pre-mix of commercially available 5 ml PEDOT:PSS (1.3 wt.%; Sigma-Aldrich) aqueous suspension with 120 µl of glycerin, 250µl of N-methylpyrrolidone, and 6.25 ml of isopropyl alcohol (IPA).

3) Figure 4-6 shows very strange effect: the shape of EQE spectra changed dramatically due to top electrode material variation, though the absorber material stays the same. Shift of the maximum by 50 nm is especially spectacular. What is the origin of this effect? Similar effect is also seen in figure 4-13, showing a great spectral change after applying a reflecting mirror on the device back side. Since simulated spectra are given, explanation of the effect (as well as a detailed description of the techniques used for simulation) needs to be provided.

Answer: The EQE spectra is shown in Figure 4-7c. The explanation for the shift is as follows:

The shift mainly arises due to optical and electrical changes. SWCNTs have absorbance in the whole spectral range (near UV to far IR, 170 to 3000 nm) with a strong plasmon peak near 250 nm as shown below in Figure 1. In our cell structure, the a-Si:H (n~4) is sandwiched between lower refractive index (n) materials (PEDOT:PSS-SWCNTs composite, $n_{PEDOT:PSS}$ = 1.2 and n_{SWCNT} = 1.09) and Al doped ZnO (n_{AZO} = 2) thereby causing interference. When the light is incident on the solar cell, it passes through a stack of layers with different refractive index. With each passing layer, the incident light transmits through much reduced intensity and phase shift at every incident wavelength. This follows similar as Fabry-Perot interferometer. Therefore, this shift at each wavelength results in a strong shift as observed in the EQE spectra in Figure 4-7c. Moreover, in Figure 4.7c for SWCNTs/a-Si:H HSC, the SWCNTs film have a non-uniform contact with underneath a-Si:H creating voids, which are filled with the insertion of PEDOT:PSS in the SWCNTs network (as shown in surface morphological SEM Figure 4-5). This results in a continuous junction with improved interface and reduced recombination. This is clearly seen in Table 4-1, with higher V_{oc} values for PEDOT:PSS-SWCNT/a-Si:H HSC when compared to SWCNTs/a-Si:H or PEDOT:PSS/a-Si:H.

In Figure 4-13 with the reflective back mirror, the incident light that transmits through the solar cell, reflects back to the solar cell stack with air in between the mirror and solar cell. The difference in the refractive index causes interference and phase shift when the light re-enters the solar cell from rear side. At this point, the light at first is incident to a glass coated with textured Al doped ZnO (thus having several internal reflections that once gain causes interference and several phase shifts at each wavelength) before getting absorbed in silicon again. This phenomenon results in a strong shift in EQE spectra.

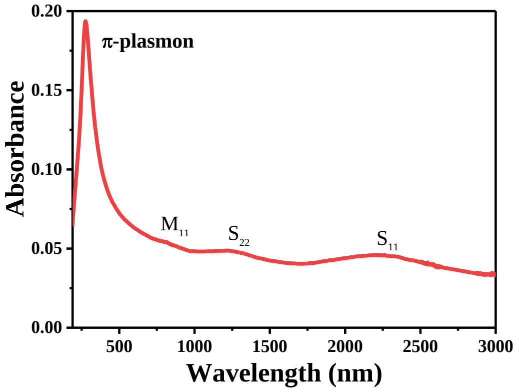

Figure 1. Absorbance spectra of SWCNT thin film utilized for adhesion studies

The text has been accordingly modified on Page 48 as:

"Additionally, the SWCNT/a-Si:H solar cell shows a strong blue-shift which may arise from the strong absorbance of SWCNTs near 250 nm [54] and phase shift of incident wavelength caused by stack of different refractive index materials in the solar cell. Moreover, in Figure 4.7c for SWCNTs/a-Si:H HSC, the SWCNTs film have a non-uniform contact with underneath a-Si:H creating voids, which are filled with the insertion of PEDOT:PSS in the SWCNTs network (as shown in surface morphological SEM Figure 4-5). This results in a continuous junction with improved interface and reduced recombination. This is clearly noted in Table 4-1, with higher Voc values for PEDOT:PSS-SWCNT/a-Si:H HSC when compared to SWCNTs/a-Si:H or PEDOT:PSS/a-Si:H."

The details of the numerical simulation is given in section 4.3.3, page 60 as follows: "numerical simulations carried out using AFORS-HET (automat for simulation of heterostructures) software." It should be noted that numerical simulations was carried out by our collaborator (DLR Institute, Germany) using AFORS-HET (automat for simulation of heterostructures) software. The simulation is detailed in Publication 3.

Some technical issues:

4. Page 11 "solar photovoltaics" better replace with "photovoltaics"

Answer: The suggestion has been addressed and modified in section 1, page 19 as: "photovoltaics".

5. Page 12 The claim "They are categorized as fourth generation PV devices and are termed 'hybrid solar cells (HSCs)'." needs to be supported with the reference. There are three commonly accepted generations of PV technologies, which are differentiated by the cost of the produced energy. Generation 3 is currently emerging. Flexible solar cells based on a-Si fall in generation 1 according to the common criteria.

Answer: The suggestion has been addressed and modified in section 1, page 20 as: "are termed as 'hybrid solar cells (HSCs)'".

6. Page 12 The claim "An energy efficient, environmentally friendly and low cost process technology is developed for fabrication of hybrid thin film solar cells combining a-Si:H and SWCNT films" is very demanding. Analysis of product embodied energy, life cycle and cost structure are needed to support such strong statements.

Answer: The suggestion of the reviewer is well appreciated and considered for future work. But, it is to be noted that in the existing standard industrial process for amorphous silicon solar cell fabrication hazardous source gases like diborane, silane, and hydrogen for p-type layer are used followed with a sputtering process of ITO, and final metallization with Al or Ag. However, in this work, the devices are fabricated under low temperature and partial atmospheric conditions (p-type TCF only, while other layers are deposited in vacuum. Hence 'partial atmospheric conditions'). And, moreover the use of hazardous source gases, expensive vacuum processing like PECVD, sputtering, and evaporation are eliminated. Thus, in this context the claim of energy efficient, environmentally friendly and low cost process technology is well justified.

7. Page 15 "to overcome their limitation" needs clarification: what is "their?"

Answer: The suggestion is addressed and accordingly the text is modified on page 23 as: "the limitation of HSC efficiency".

8. Page 15 terminology “has a higher absorption edge and a larger optical absorption constant than c-Si.” Looks not precise. Revise using e.g. has lower band gap, higher extinction coefficient, becomes direct band gap material…

Answer: The suggestion is addressed and accordingly the text is modified on page 23 as: The a-Si:H has a larger mobility gap and optical absorption coefficient than c-Si.”

9. Page 15. Wording “The mobility gap of a-Si:H is larger than the bandgap of single crystal silicon and has a typical value between 1.7 eV and 1.8 eV [11]. Therefore, just 1 µm in thickness of a-Si:H is sufficient to absorb virtually all of the light above the absorption edge [11].” is very misleading. Extinction coefficient and direct band gap structure should be mentioned. Above absorption edge usually means at longer wavelengths, while the intended meaning is just opposite.

Answer: The sentence is revised on page 23 as suggested: “The mobility gap of a-Si:H is larger than the bandgap of single crystal silicon and has a typical value between 1.7 eV and 1.8 eV [11]. Therefore, just 1 µm thickness of a-Si:H is sufficient to absorb virtually all of the incident light that is ≥mobility gap [11].”

10. Page 20 “through the doping of polar solvents, strong acids, ionic liquids”. To keep terminology correct, this is not doping, it is modification.

Answer: The suggestion is addressed and accordingly modified on page 28 as: “the modification”

11. Page 22. Statement “In addition to that, the film thickness can be easily estimated when the absorbance is known” is not fully correct since absorption coefficient is needed. Moreover, light interference effects can affect the accuracy of the measurements.

Answer: The thickness of the SWCNT films calculated from their absorbance is given by:
Thickness (nm) = 417 × $\text{Absorbance}_{550\text{ nm}}$. The details are given in Mikheev, G. M.; Nasibulin, A. G.; Zonov, R. G.; Kaskela, A.; Kauppinen, E. I. Photon-Drag Effect in Single-Walled Carbon Nanotube Films. Nano Lett. 2012, 12 (1), 77−83.

The text is modified on Page 43 as “(as described in section 3.1)” and section 3.1, Page 31 as follows: “In addition to that, the film thickness can be easily estimated when the absorbance is known as following: Thickness (nm) = 417 × Absorbance550 nm [67].”

12. Page 28 typing “would leads to”

Answer: The suggestion is addressed and accordingly the text is modified on page. 37 as: “would lead to”.

13. Page 32. The statement “The experimentally measured adhesion force shown in Figure 4-2d can explain the following observations: SWCNT thin films are easily dry-transferred onto a-Si:H, Si, SiO2, and PDMS in air, while under the same conditions their transfer onto ITO and Pt is complicated and completely failed on ZrO2.” Is not really clear. Figure 4-2 shows virtually identical AF values for SiO2 and Pt in air. Why then SWNT transfer on SiO2 is easy, while on Pt it is complicated?

Answer: In this work, quantitative measurement of randomly oriented SWCNT films adhesion with various materials was studied and a mechanism is proposed for improving the adhesion. However, apart from the surface functionalization and atmospheric conditions, the surface roughness of the substrate is also very critical in the adhesion of SWCNTs. This study is a continuing future work. To the benefit of the reviewer, in this work too, the surface roughness of the substrate was found as the first parameter to influence the adhesion. Hence, it is possible that the SiO2 (glass) surface has lower roughness than Pt (metal) due to which SWCNTs could be easily transferred on SiO2 but complicated on Pt, although the AF values are identical.

14. Page 33. I would not use term “fluorination” for HF treatment. The statement “Moreover, after the fluorination process SWCNT films can be easily dry-transferred even onto problematic materials, such as ITO, Pt, and ZrO2.” is not clear. AF for HF-treated ZrO2 is still below the value for Pt (not HF-treated) in air, which was called problematic on the previous page. Is there any AF values range to characterize “easy”, “problematic” and “completely failed”? I aslo recommend to explain “HF-treatment” in the caption of Figure 4-2

Answer: The suggestion has been addressed and accordingly modified on page 42 as: “(HF-treated) and (HF-treatment)”. The terminologies used are categorized as “easy”, “problematic”, and “completely failed” based on the reproducible observation in the conducted experiments. The term “easy” is when the SWCNTs are completely transferred onto a substrate without any process, “problematic” is in the case when the SWCNTs are partially transferred onto a substrate and require a process (densification), and “completely failed” is when the SWCNTs do not transfer at all onto a substrate. The HF-treatment is explained on page 34 and referred to figure 4-2 in the same paragraph.

15. Page 35 Statement “The decrease in the sheet resistance of the SWCNT-PEDOT:PSS (composite) film and the increase in its work function compared to the pristine SWCNT film can account for the fact that the PEDOT:PSS filled micropores in the film and, consequently, doped the SWCNTs.” is not fully clear. How can PEDOT:PSS dope SWCNTs? What is the chemistry of doping? Alternatively, can it be just contribution of PEDOT:PSS higher WF to the overall increase in the WF of the composite?

Answer: Every single carbon atom in SWCNTs is on the surface exposed to the environment. Therefore, any atom/molecule put on a SWCNT causes changes in their electronic structure and charge transfer between the atom/molecule and a nanotube[1,2]. Therefore, when PEDOT:PSS is injected on the SWCNT film, the charge carriers are transferred, thereby doping the SWCNTs and resulting in decreased sheet resistance as in Figure 4-4. Further, the KPFM measured work functions are similar to the ultraviolet photoemission spectroscopy measured values as reported by Fan *et al.* [3].
The text has been accordingly revised on Page 44 as follows:

“Fan *et al*. reported similar values of work functions measured by ultraviolet photoemission spectroscopy [97]”, and “every single carbon atom are on the surface exposed to the environment. Therefore, any atom/molecule put on a SWCNT cause changes in their electronic structure and charge transfer between the atom/molecule and a nanotube. Therefore, when PEDOT:PSS is injected it filled micropores in the SWCNT film and, that the holes in the PEDOT:PSS patches can transfer to the interconnected SWCNT network consequently, doping the SWCNTs [56,57,97]”.

References:
[1] Kim KK, Yoon SM, Park HK, Shin HJ, Kim SM, Bae JJ, et al. Doping strategy of carbon nanotubes with redox chemistry. New J Chem 2010. https://doi.org/10.1039/c0nj00138d.
[2] Ki KK, Jung JB, Hyeon KP, Soo MK, Geng HZ, Kyung AP, et al. Fermi level engineering of single-walled carbon nanotubes by AuCl 3 doping. J Am Chem Soc 2008. https://doi.org/10.1021/ja8038689.
[3] Fan Q, Zhang Q, Zhou W, Xia X, Yang F, Zhang N, et al. Novel approach to enhance efficiency of hybrid silicon-based solar cells via synergistic effects of polymer and carbon

nanotube composite film. Nano Energy 2017. https://doi.org/10.1016/j.nanoen.2017.02.003.

16. Figure 4-5 What is “Morphological SEM image”?

Answer: Figure 4-5 title text is modified as: “Surface morphological SEM image”.

17. Table 4.3 Giving efficiency values with the extreme accuracy such as “2.704” might be misleading. I suggest to give it as 2.7% only. Usually, some statistics is given (average +/-) in such tables and number of cells in the batch contributing to the average is indicated in the footnote to the table.

Answer: Table 4.3 is modified as follows:

Conditions	V_{oc} **(V)**	J_{sc} **(mA/cm^2)**	**FF (%)**	**η (%)**
without PMMA	0.820	7.90	41.5	2.70±0.01
with PMMA	0.896	8.99	41.8	3.40±0.01

Reply to Prof. Anvar Zakhidov comments:

Q. The reference a-Si:H cells show much lower performance when compared to the best recorded cells. I suggest to discuss the reasons for this discrepancy in the thesis and during the defence.

Answer: We received the a-Si:H structures till the intrinsic absorber (from collaborator, DLR Institute, Germany) for which the reference cell produced in their baseline process production line had PCE of stable 7.5%. The hybrid heterostructure solar cells using the proposed TCF was fabricated with the received a-Si:H samples. It is to be kindly noted that the reference a-Si:H cell produced for this work was at lower deposition temperature (< 200 °C), without any back reflector, special texturing etc. Moreover, the goal of this thesis was not to produce world record a-Si:H solar cells. In this study, we used simple low temperature processes to establish a proof of concept with SWCNTs as p-type transparent conductor.

The text is modified on section 4.3.3, Page 61 as follows:
“It is to be noted that the reference cells are produced at substrate temperatures less than 200 °C, without any back reflector, texturing and other special processes as carried out for record a-Si:H solar cells.”

Q. However, it is suggested that the candidate highlights some of the possible future work, as the extension of this important study in the last section of his thesis.

Answer: The possible future work are briefly described in the last section (conclusion and future work). The scaling of the proposed TCFs is the ultimate goal. But, for that to happen successfully, it is necessary to address several scientific and technological bottlenecks. They include: synthesis of reproducible and uniform SWCNTs, uniform doping of SWCNTs over large area samples, stability of conductive polymers, and finally a stable encapsulant.

The text is modified on Page 65 as follows:

“It is envisaged that the outcomes of this work will secure the future development of novel p-type TCFs in combination with the use of pure high quality semiconducting or metallic SWCNTs that are aligned with better passivation, improved doping stability of SWCNTs, light trapping schemes and nanostructuring that can potentially improve future photovoltaic devices.”